THE DETERMINATION OF TRACE METALS

Ontario

Ministry
of the
Environment

Laboratory
Branch

DATED

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THE DETERMINATION OF TRACE METALS

Metal Analysis by Atomic Absorption Spectrophotometry

Atomic absorption methods can be applied to virtually all elements. However, only for certain elements is the sensitivity adequate.

At present only *16* listed elements are routinely determined by atomic absorption procedures in this laboratory. The elements are aluminum, cadmium, calcium, chromium, cobalt, copper, iron, lead, lithium, magnesium, manganese, molybdenum, nickel, silver, strontium and zinc. *Five* others, barium, gold, tin, titanium, & vanadium are determined on a non routine basis.

Aluminum

Aluminum is the *third* most abundant element in the earth's crust and is present in virtually all natural waters, as a soluble salt or colloid.

The metal is used extensively in domestic utensils, wire, exterior building finishes and in any industrial applications where a strong, light, easily constructed material is needed.

The element does not appear to be essential to plants, animals or micro-organisms and does not accumulate to any great extent in plant or animal tissues.

Oral toxicity of aluminum and aluminum salts seems to be negligible although ingestion of large amounts alters the body's method of inorganic phosphate elimination. Inhalation of the element or its salts can cause lung problems.

Barium

Barium, as an alkaline earth occurs widely in nature in lower concentrations and in similar locations to strontium. Industrially, it is used in alloys, plating, ceramics, glass and in the manufacture of salt water concrete.

Barium salts are retained in muscle tissue and more specifically bone marrow, but no conclusive evidence of its necessity for human survival has appeared. Ingested barium salts are quite toxic in large doses causing gastroenteritis and paralysis.

The Ontario drinking water objective is *1 mg/l Ba*.

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Cadmium

Cadmium metal is deposited electrolytically from a solution of its cyanide complex to form a protective coating for iron and steel. It is also used as an alloy in automatic fire extinguishers and in automobile bearings. Cadmium compounds form a series of valuable yellow-to-red pigments used in paints and printing inks. Cadmium may enter waters as a result of industrial discharge or from the deterioration of galvanized pipe.

The metal accumulates as a metalloprotein complex in the liver and kidneys. Excess intake of cadmium can result in hypertension.

Cadmium has high toxic potential, having been implicated in some cases of food poisoning. Minute quantities of cadmium are suspected of being responsible for adverse renal arterial changes in human kidneys. A cadmium concentration of *0.20 mg/l* has been toxic to certain fish. On the other hand, there is an indication that cadmium might possibly be a dietary essential. The concentration in drinking water has been reported to vary between *0.0004 and 0.06 mg/l*, with a mean of *0.0008 mg/l*. The maximum permissible concentration of dissolved cadmium in drinking water is *0.01 mg/l*.

Gold

Gold is widely used in jewellery and as a currency standard.

It is rarely found in significant quantities in waters, sediments, plant or animal tissue.

Calcium

Calcium chloride is deliquescent and is useful as a household dehumidifier and in reducing dust on unpaved roads. The saturated water solution freezes at *-48°C* and as such is useful as an anti-freeze agent and refrigerant. Gypsum $(CaSO_4 \cdot 2H_2O)$ is a necessary ingredient of Portland cement; when heated gypsum forms plaster of Paris which when moistened with water swells and resets in about *half an hour* to a solid mass of gypsum. Calcium carbide is an important source of acetylene. When calcium carbide is heated in an electric oven in the presence of nitrogen, it is converted to calcium cyanamid, a fertilizer.

The calcium content of water may range from *zero* to *several hundred mg/l* depending on the source and treatment.

Small concentrations of calcium carbonate combat corrosion of metal pipes by depositing a protective coating. Appreciable levels of calcium salts, on the other hand break down on heating to form harmful scales in boilers, pipes and cooking utensils.

The element is found in relatively high concentrations in the human body. Calcium carbonate is a major component of bones and teeth. The aquated ion effects the electrochemical processes of nerve impulses, acts as a solubilizing agent for proteins and is involved in the activation of many enzymes.

Cobalt

The element occurs in the minerals cobaltite, smaltite and erythrite and is obtained from nickel, lead, copper and iron ores.

The element is magnetic and is used in magnetic alloys, and in other alloys and electroplating. The trivalent salts have an intense blue colour and have been used for centuries in glazes and glasses. A radioactive cobalt isotope Co^{60} has been used in cancer treatment.

Cobalt is essential in human and animal nutrition because it is the central atom in the vitamin B_{12} complex. Cobalt, and thus B_{12} deficiencies cause emaciation and listlessness, loss of appetite and anemia. As the body does not accumulate cobalt to any extent, a regular intake is necessary. Cobalt augmented feeds are often required for cattle and other ruminant animals as their systems are extremely inefficient in synthesizing the vitamin from ingested cobalt.

A dose of *0.5 gm* may be lethal while daily *5 mg* doses may cause palpitations, a rise in blood pressure and other effects.

Copper

Copper salts are used in controlling growths in reservoirs, for catalyzing the oxidation of manganese, and for controlling slime in distribution systems. The corrosion of copper, brass and bronze pipe and fittings may result in the introduction of measurable concentrations of copper into a water system.

Copper is an essential element to the human body, acting as a catalyst in many biochemical reactions. Large oral doses may, however, produce emesis and if prolonged, may result in liver damage, anemia and several other diseases.

Copper poisoning occurs more often in grazing livestock than in man, usually resulting from consumption of dry feeds and grasses containing high copper concentrations. Molybdenum acts to rid the body of excess copper and provision of salt licks containing ammonium molybdate can prevent the onset of the symptoms of copper poisoning, hemolysis and jaundice. The free, aquated copper ion is extremely toxic to fish. When bound by organic liquids the metal is biologically less active.

Amounts above *1.0 mg/l* can impart a bitter taste to the water. The natural copper content of water seldom exceeds *0.6 mg/l* and generally falls below *0.03 mg/l*. The maximum permissible concentration of dissolved copper in drinking water is *1.0 mg/l*.

Iron

The pure form of iron is not used very much in industry, but it is processed to cast iron, wrought iron, or steel for industrial purposes.

Iron is an essential element in human nutrition, being the central atom of the heme group which transports oxygen throughout the body. Iron is stored in the body as ferrotin and hemosiderin compounds which are found primarily in the spleen and bone marrow. Iron deficiency leads to listlessness and fatigue and in children to anorexia and depressed growth. An adult male requires *10 mg* of iron/day.

Natural waters contain variable but minor amounts of iron. Surface waters seldom contain in excess of *1 mg/l* iron. Some ground waters and acid surface waters may contain considerably more. Iron concentration above *0.30 mg/l* imparts a taste to drinking water and causes staining problems to laundry and porcelain. Iron oxide particles are sometimes collected with a water sample as a result of flaking of rust from pipes. The maximum permissible concentration of dissolved iron in drinking water is *0.30 mg/l*.

Lead

Lead and its oxides are used in storage-battery plates, in roofs, and in alloys. A self-sealing oxide film that forms over lead in air makes it relatively resistant to atmospheric corrosion or corrosion by oxygen-bearing waters. Thus it is used widely in pipes, cable sheathing, and protective coatings on structural steel. Tetraethyl lead is used as an anti-knock agent in gasoline. Its presence in a water supply may arise from industrial, mine and smelter discharges, or from the dissolution of old lead plumbing. Tap waters which are soft, acidic and not suitably treated may contain lead arising from an attack on the lead service pipes.

Lead is a cumulative body poison and is to be avoided. Although human consumption from lead pipes and similar materials has decreased in recent years, ingestion from automobile exhausts and smelting operations has increased so that the average daily intake is well above the preindustrial or natural levels.

Lead is eliminated slowly from the body in the feces and indications of increasing bodily concentrations with age in average male subjects suggests that in our present urban environments, excretion is not keeping pace with ingestion. Children, with higher consumption per pound than adults are particularly susceptible to lead poisoning. Biochemical experiments have indicated that elevated lead concentrations affect protein and enzyme synthesis.

Acute lead poisoning is manifested by colic, anemia and brain damage. Natural waters seldom contain more than *0.02 mg/l*, although values as high as *0.4 mg/l* have been reported. The maximum permissible concentration of dissolved lead in drinking water is *0.05 mg/l*.

Lithium

The element does not occur free in nature but is combined in small amounts in nearly all igneous rocks and in the waters of many mineral springs. The metal is used in alloys, organic syntheses and special glasses. Lithium chloride and lithium stearate are very hygroscopic and thus used in dehumidifiers. (Lithium hydride is extremely corrosive and irritating.)

Lithium salts occur in traces in the body and have an effect on mineral balance, by replacing sodium ions. At this time, the element is not thought to be essential to either plant or animal life. Lithium salts have been used extensively in the treatment of mania, where the medication produces a calming effect without producing listlessness.

Magnesium

Because of its lightness, magnesium is used in lightweight machinery, and portable tools and devices. Since the metal ignites readily in wire or powder form, it is used in signal flares, photographic flash bulbs and pyrotechnics. Magnesium also reacts with oxygen and nitrogen and is used to rid vacuum tubes of these gases. A suspension of magnesia in water is known as "Milk of Magnesia" and is used as a neutralizer of stomach acids and as a laxative. "Epsom Salts" (magnesium sulphate) is used as a cathartic.

Important contributors to the hardness of water, magnesium salts break down on heating to form deleterious scale in boilers. Concentrations in excess of 125 mg/l can also exert a cathartic and diuretic action. Magnesium concentrations may vary from zero to several hundred mg/l depending on the source and treatment of the water.

The element is essential to plant and animal life. Magnesium is the central atom in the chlorophyll molecule. It is also involved in the basic electrochemical processes of the body, regulating cell membrane permeability, and in catalysis, being the most common enzyme activator.

Manganese

Manganese containing minerals are widely distributed, oxides, silicates and carbonates being the most common. The metal forms many important alloys, improving the strength, toughness, wear resistance and hardness of steels. Manganese dioxide is used in the preparation of oxygen and chlorine and as a depolarizer in dry cells.

Manganese is essential in plant and animal nutrition. The minimum human requirement is between 3 and 9 mg daily. Manganese deficiency in animals results in impaired growth, skeletal abnormalities, depressed reproduction and alaxia of the newborn. Biochemically, the element plays a part in lipid and carbohydrate metabolism.

Although manganese is among the least toxic of the trace elements to animal life, prolonged exposure to manganese containing ducts (as in mines) causes severe poisoning, effecting motor facilities such as speech, arm and leg movements.

Molybdenum

Molybdenum is obtained primarily from 2 ores, molybdenite and sulfenite. The metal is an important alloying agent in steel, providing hardness and toughness. Molybdenum sulphide is an excellent high temperature lubricant.

Molybdenum is essential in plant and animal nutrition. It interacts with copper in the body, altering bodily copper concentrations in a complicated manner. The other biochemical function of molybdenum known at this time is in the formation and activity of xanthine oxidase, a protein essential to the nitrogen fixing process.

Nickel

Seventy percent of the Western nations' nickel is obtained from ores in the Sudbury region. It is used in corrosion resistant alloys, as a hydrogenation catalyst, in nickel-cadmium batteries, and in coins.

Orally administered doses of nickel salts are non toxic. Contact with the metal can cause a severe form of dermatitis. Nickel tetracarbonyl, a compound formed in the purification of the metal, is extremely toxic and may also be carcinogenic.

The element appears to be biochemically active, activating several enzyme systems, and appearing in high concentrations in ribonucleic acid.

Silver

The element occurs in the ores argentite (Ag_2S) and horn silver ($AgCl$). It is usually found in lead-zinc and copper-nickel ores.

The metal, being the best thermal and electrical conductor know, is used in printed circuits and electrical contacts. Some silver salts are photosensitive and are used extensively in photographic processes.

Doses of colloidal elemental silver are cumulative, causing death or blindness. Constant handling of the metal or its salts can cause skin discolouration and eye lesions.

Strontium

The element occurs naturally as celestite ($SrSO_4$), strontianite ($SrCO_3$) and apatite. It is present in sea water (*10 mg/l*) and most plant tissues.

The metal is used in lead alloys to add hardness and durability. Strontium sulphate is used in paints, the chloride is used in freezing mixtures and refrigerators. The radioactive isotope Sr^{90} is one of the best high energy β-emitters known, and thus provides a light-weight, long lived nuclear electric energy source.

The radioactive isotope is a product of nuclear explosions and can present a health problem. The toxicity to animals is slight, about the same as calcium.

The element accumulates in bones and certain plants. There is some evidence that strontium is important in the process of bone and tooth calcification.

Tin

The element occurs in nature chiefly as the oxide SnO_2. Industrially, it is used in tin plate, alloys and as a chemical reducing agent. Organotin compounds are used as stabilizers in polyvinyl plastics and chlorinated rubber paints, also as fungicides, insecticides and anthelmintics for poultry.

The element and its inorganic salts are not accumulated in the body and are essentially non-toxic. Organotin compounds, particularly diethlyl, tin, can cause severe lesions and even death.

Titanium

Titanium is the *8th* abundant element in the earth's crust, present in most soils from *0.5-10%*. Neither plants nor animals accumulate the element to any extent, the concentration in soils being usually *10,000* times greater than in uncontaminated herbage. There is no evidence that the element plays an essential role in human or animal nutrition.

The element is used in many alloys such as ferrotitanium and lamp filaments. The oxide is used as a white pigment in paint and the tetrachloride and the natural oxides (rutile and ilmenite) are used in ceramics and glass.

Titanium salts are used extensively in the treatment of skin disorders.

Vanadium

Vanadium is found in soils ($\approx$ *.03%*) and plants (*1 ppm*). It is also widely distributed in human and animal tissues. The salts of this element have recently been discovered to be essential to human life, being involved in body redox reactions. Vanadium also inhibits the synthesis of cholesterol.

The element is not particularly toxic to human life in the dissolved form. Industrial poisonings have occured however from inhalation of vanadium pentoxide dust. The element is used in alloys and the pentoxide is used as a catalyst in the manufacture of sulphuric acid, dyes and inks.

Vanadium is also found in all fuel and motor oils and has been used for oil spill identification by means of the nickel vanadium ratio.

Zinc

Zinc is relatively resistant to atmospheric corrosion and is used as a protective coating on iron and steel; the product is known as galvanized iron. Zinc is also used in dry cell batteries and in a variety of alloys, notably brass and die-casting alloys. Zinc salts are toxic to micro-organisms and are used as wood preservatives and disinfectants. Zinc oxide is used in medical ointments and as a pigment; the carbonate and sulphide are used as white pigments in paints and enamels. Zinc sulphide is also widely used as a Phosphor for television screens and fluorescent coatings. Zinc most commonly enters the domestic water supply from the deterioration of galvanized iron and the leaching of brass. Zinc may also appear as a result of industrial waste pollution.

Zinc is essential to plant and animal life. Deficiencies result in growth retardation, skin lesions, bone weaknesses, poor healing of wounds, impaired reproductive processes and reduced learning capacity.

Biochemically, zinc is involved in nucleic acid and protein synthesis, carbohydrate metabolism, enzyme activity and hormone production.

The average daily intake is *12-15 mg*. The element is relatively non toxic, criteria being based on unpalatibility rather than toxicity.

Concentrations above *5 mg/l* can cause a bitter astringent taste and an opalescence in alkaline waters. The zinc concentration of drinking water has been reported to vary between *0.06 mg/l and 7.0 mg/l* with a mean of *1.33 mg/l*. The maximum allowable concentration of dissolved zinc in drinking water is *5.0 mg/l*.

1. Sample Handling and Preservation

A *100 ml* sample is sufficient for all Atomic Absorption analyses. As repeats are sometimes required or if pre-concentrations are necessary, a *500 ml* sample is preferred.

Acid preservation minimizes absorption and precipitation effects. Correct choice of sample container is necessary to prevent serious absorption and desorption errors. See Table I.

2. Selection of Method

The choice of digestion procedure is a function of the sample matrix and the chemical properties of the element or combination of elements which are to be analyzed.

The digestion procedure must remove all organic material and solubilize the metal salts and oxides present.

Samples containing large amounts of protein such as fish muscle are digested with nitric and perchloric acids. This digestate is suitable for AAS analysis for all metals. Because of the danger of explosions with perchloric acid, this method is used only when necessary.

The hydrochloric-nitric (aqua regia) digestion is superior for the determination of lead, barium, calcium, magnesium, tin and gold. It is unsuitable for chromium and iron because of the possibility of loss of volatile chlorides. Silver chloride is very insoluble, thus the aqua regia digestion is not suitable for this element. Iron, chromium and silver and analyzed after sulphuric-nitric digestion.

The other elements can be determined after either digestion procedure, the choice depending on the combination of the elements and the restrictions above.

After the initial digestion step, a single atomic absorption analysis requires less than *1 ml* of sample, takes only a *few seconds* to perform and is relatively free of interferences.

Thus, where the techniques has adequate sensitivity for a particular element, it is the method of choice.

TRACE METALS DETERMINATION

ATOMIC ABSORPTION SPECTROPHOTOMETRY

SUMMARY	
Substance determined.	*Al, Au, Ba, Ca, Cd, Co, Cu, Cr, Mg, Mn, Mo, Ni, Fe, Pb, Li, Ag, Sr, Sn, V, Ti, Zn.*
Interpretation of results.	Results reported as the element in *mg/l*.
Principle of method.	An aliquot of sample is prepared either by wet oxidation or dry oxidation followed by fusion and leaching to render it suitable for aspiration into a flame. The metal ions are reduced to free atoms by the reducing zone of the flame. Atoms in the elemental state absorb energy of very specific wavelengths which are different for each element. An atom of aluminum, for example, will absorb energy provided by a hollow cathode lamp which emits the elemental spectrum of aluminum. The energy absorbed is directly proportional to the concentration of atoms in the original system.
Time required for analysis.	A single digestion requires about *half a day*. About *20* can be done at one time in batches. An individual AAS analysis for a single element requires only *a few seconds*. However, changing lamps, machine set up, organizing and reporting requires considerable time.
Range of application.	See Table I.
Standard deviation.	See Table I.
Accuracy.	See Table I.
Limit of detection.	See Table I.
Interferences and Shortcomings.	AAS techniques are relatively free of interferences, however stable compound formation, incomplete volatilization, matrix effects, scatter and background

SUMMARY	
Interferences and Shortcomings. continued.......	absorption can all occur. These effects can be suppressed by the addition of certain reagents or by a background correction using a non-absorbing wavelength.
Minimum volume of sample.	See Table I.
Preservation and sample container.	See Table I.
Safety considerations.	Extreme care should be taken in the handling and use of the various concentrated acids especially aqua regia and perchloric acid. Digestions should be carried out in a well ventillated fumehood. Wear eye protection at all times when digesting samples or handling acids. The atomic absorption unit should have a proper exhaust canopy to expel the heat and fumes. Ensure that the gas cylinders are properly secured to the bench top. Ensure that the proper instructions for the operation of the atomic absorption unit are followed especially ensuring that the waste trap is filled with water at all times and the fuel is shut off first.

TABLE I

A.A.S. SAMPLE HANDLING AND ACCURACY PARAMETERS

	Volume Required in ml *	Sample Container **	Preservative	Detection Limit (mg/l) ***	Standard Deviation mg/l ***	Accuracy mg/l	Range mg/l
ALUMINUM	200	glass or plastic	HNO_3 (10 drops)	0.10	.02 at 1.0	.03 at 1.0	.1 - 10
BARIUM	100	" "	" "	0.02	--	--	.02 - 20
CALCIUM	100	" "	" "	0.05	--	--	.05 - 5
CADMIUM	100	" "	" "	0.01	.004 at 0.1	.008 at 0.1	.02 - 2
COBALT	100	" "	" "	0.07	--	--	.07 - 7
COPPER	100	" "	" "	0.05	.015 at 0.3	.01 at 0.3	.05 - 5
CHROMIUM	100	" "	" "	0.01	.03 at 0.5	.01 at 0.5	.01 - 1
GOLD	100	" "	" "	0.02	--	--	.02 - 10
MAGNESIUM	100	" "	" "	0.004	--	--	.004 - 4
MANGANESE	100	" "	" "	0.04	.01 at 0.2	.1 at 0.2	.04 - 4
MOLYBDENUM	100	" "	" "	0.03	.02 at 1.0	.02 at 1.0	.03 - 3
NICKEL	100	" "	" "	0.07	.03 at 0.5	.1 at 0.5	.07 - 7
IRON	100	" "	" "	0.06	.10 at 1.0	--	.06 - 6
LEAD	100	" "	" "	0.12	.09 at 1.0	.7 at 1.0	.12 - 12
LITHIUM	100	" "	" "	0.001	.002 at 0.1	--	.001 - 1
SILVER	100	" "	" "	0.04	--	--	.04 - 4
STRONTIUM	100	" "	" "	0.004	--	--	.004 - 4
TIN	100	" "	" "	0.4	.8 at 20	--	.4 - 50
TITANIUM	100	" "	" "	0.08	--	--	.08 -
VANADIUM	100	" "	" "	0.07	.04 at 1.0	--	.07 - 50
ZINC	100	" "	" "	0.05	.05 at 0.5	.01	.05 - 5

* If all the parameters are requested, then a 200 ml sample is sufficient. If preconcentration is required then a 1,000 ml sample should be submitted.

** Glass containers must have Teflon lined caps.

*** Detection limit and standard deviations vary somewhat between instruments.

TRACE METALS ANALYSIS

ATOMIC ABSORPTION SPECTROPHOTOMETRY

1. Introduction

Atomic absorption spectrophotometry is an analytical technique for the determination of elements based on the absorption of radiation by free atoms. The production of atoms from a chemical compound requires the absorption of energy. The energy is usually supplied in the form of heat from a flame. The absorption of thermal energy from the flame, with a subsequent emission of the energy as a spectral line, corresponds to atomic emission. Atomic absorption corresponds to the absorption of energy from a source other than the flame (usually the signal from a hollow cathode lamp) with the subsequent decrease in the signal from the source. To determine total or leachable elements, the sample aliquot is either digested, leached or fused (after dry ignition). This preparation breaks down any organic matter, solubilizes any particulate matter and if the matter cannot be dissolved, stabilizes it prior to filtration. After the proper preparation of sample, the resultant solution should be clear and colorless (as far as possible).

2. Interferences and Shortcomings

Because of the simplicity of absorption spectra, there are very few known examples of actual spectral interferences. Interferences which actually influence the proportion of atoms in the flame available to absorb the resonance radiation arise largely from the chemical effects which originate in the flame itself, or in the sample solution. Such interferences are caused by the formation of stable compounds or by ionization.

In addition, minor interferences are caused by various physical phenomena, including incomplete volatilization of the solid particles formed in the flame, variations in the physical properties of solutions (matrix effects), scatter and background absorption.

(a) Chemical Interferences:

(1) Stable Compound Formation

This arises because compounds or radicals containing the element being measured are not broken down into individual atoms at the temperature of the flame being used. Stable compounds can even be formed in the flame. Examples of this are:

(i) The lowering of alkaline earth metal absorbances in the presence of large excesses of aluminate, silicate, phosphate and some other oxy-anions.

A releasing agent such as lanthanum chloride is added which forms stable oxy-salt complexes thus freeing the alkaline earth ions and facilitating their reduction.

(ii) Metals which form refractory oxides (Al, V, Si, Ti) have low sensitivity.

A combination of the high temperature reducing N_2O-C_2H_2 flame and the addition of large excesses of elements which also form stable oxides and thus compete for the available oxygen in the flame, increases sensitivity.

(iii) The calcium signal is depressed in the presence of protein. This is compensated for by a thorough sample digestion.

(2) Ionization

Many metals, including aluminum, silicon and chromium, are ionized to an appreciable extent at the hot flame temperatures of nitrous oxide-acetylene. A potassium or lithium concentration of approximately *1000 mg/l* will usually minimize this ionization effect.

(b) Physical Interferences

(1) Incomplete Volatilization

This implies that, at the flame temperature used, the droplets produced by the nebulizer have given rise to solid particles which, because of their vaporization temperature or speed through the flame, or both, are not completely converted to a vapour. This type of interference is usually caused by the formation of metal-metal solutions of high boiling point under reducing conditions. An example of this is the depression of the chromium signal in the presence of high iron concentrations in an air-acetylene flame. This type of interference is non-existent in a nitrous oxide-acetylene flame.

(2) Matrix Effects

These influence the number of atoms actually entering the flame, and arise from differences in physical properties of the sample. This can be caused by varying the acid concentrations which in turn can cause a difference in viscosity or surface tension. In order to help compensate for this effect, samples, standards, and blanks should be made up to the same acid or salt concentration.

(3) Scatter and Background Absorption

This is the result of either small solid particles in the flame which scatter some of the hollow cathode radiation, or discrete molecules which absorb some incident energy.

The effect is compensated for by use of deuterium background correction or use of a non-absorbing line. Specific examples are (1) molecular absorption on the lead (2,170Å) line by calcium, magnesium, sodium and potassium, (2) molecular absorption on the nickel (2,320Å) line by calcium, (3) molecular absorption on the cadmium, (2,288Å) line by sodium chloride.

3. Apparatus

a) Atomic Absorption Spectrophotometer Varian Techtron AA4 and AA5, Perkin Elmer 503, equipped with a direct concentration readout or recorder.

b) Hot plate. Use only in a well ventilated fume hood.

c) Folin digestion tubes, graduated at 25 and 50 ml.

d) 250 ml graduated Griffin beakers.

e) Speedivap beaker covers for 250 ml beakers.

f) Glassware: Various pipets (volumetric).
Regular laboratory glassware.

g) Millipore filtration unit (glass) equipped with filters (0.45 size).

h) Acid dispensers (Oxford pipettors).

i) Thermolyne muffle furnace type 1300.

j) Graphite crucibles.

k) Crucible tongs (home-made).

l) Magnetic stirrer with stirring bars.

4. Reagents

a) Sulphuric acid, concentrated, "Aristar" (high purity grade-low in metals) or Baker "Ultrex".

b) Nitric acid, concentrated, reagent grade.

c) Hydrochloric acid, concentrated, reagent grade.

d) Perchloric acid, concentrated, reagent grade.

e) Anti-bumping granules.

f) Stock Copper Solution

Dissolve *1.000 gm* of copper wire in concentrated hydrochloric acid. Dilute to *1,000 ml* with distilled water.
1 ml = 1,000 µg Cu.

g) Stock Lead Solution

Dissolve *1.000 gm* of lead metal in concentrated nitric acid. Dilute to *1,000 ml* with distilled water.
1 ml = 1,000 µg Pb.

h) Stock Zinc Solution

Dissolve *1.000 gm* of zinc powder in concentrated hydrochloric acid. Dilute to *1,000 ml* with distilled water.
1 ml = 1,000 µg Zn.

i) Stock Cadmium Solution

Dissolve *1.000 gm* of cadmium metal in concentrated hydrochloric acid. Dilute to *1,000 ml* with distilled water.
1 ml = 1,000 µg Cd.

j) Stock Iron Solution

Dissolve *1.000 gm* of iron wire in concentrated hydrochloric acid. Dilute to *1,000 ml* with distilled water.
1 ml = 1,000 µg Fe.

k) Stock Calcium Solution

Dissolve *2.497 gm* of calcium carbonate in concentrated hydrochloric acid. Dilute to *1,000 ml* with distilled water.
1 ml = 1,000 µg Ca.

l) Stock Magnesium Solution

Dissolve *1.000 gm* magnesium ribbon in concentrated hydrochloric acid. Dilute to *1,000 ml* with distilled water.
1 ml = 1,000 µg Mg.

m) Lanthanum Solution (*10%*)

Dissolve *117 gm* of La_2O_2 (high purity) in *200 ml* concentrated hydrochloric acid. Dilute to *1,000 ml* with distilled water.

n) Stock Aluminum Solution

Dissolve *1.000 gm* aluminum wire in nitric acid. Dilute to *1,000 ml* with distilled water.
1 ml = 1,000 µg Al.

o) Stock Chromium Solution

Dissolve *1.000 gm* of chromium metal in *1:1* hydrochloric acid with gentle heating, cool and dilute to *1,000 ml* with distilled water.
1 ml = 1,000 µg Cr.

p) Stock Nickel Solution

Dissolve *1.000 gm* nickel metal in aqua regia. Dilute to *1,000 ml* with distilled water.
1 ml = 1,000 µg Ni.

q) Stock Cobalt Solution

Dissolve *1.000 gm* cobalt in *1:1* nitric acid and dilute to *1,000 ml* with distilled water.
1 ml = 1,000 µg Co.

r) Stock Lithium Solution

Dissolve *5.324 gm* lithium carbonate in the minimum volume of *1:5* HNO_3 and dilute to *1,000 ml* with distilled water.
1 ml = 1,000 µg Li.

s) Stock Silver Solution

Dissolve *1.000 gm* of clean silver metal in *10 ml* of *1:1* nitric acid and dilute to *1,000 ml* with distilled water.
1 ml = 1,000 µg Ag.

t) Stock Manganese Solution

Dissolve *1.000 gm* manganese metal in the minimum volume of *1:1* nitric acid and dilute to *1,000 ml* with distilled water.
1 ml = 1,000 µg Mn.

u) Stock Molybdenum Solution

Dissolve *1.000 gm* molybdenum metal in concentrated HNO_3 with gentle heating and dilute to *1,000 ml* with distilled water.
1 ml = 1,000 µg Mo.

v) Stock Strontium Solution

Dissolve *1.685 gm* strontium carbonate in *10 ml 1:1* nitric acid and dilute to *1,000 ml* with distilled water.
1 ml = 1,000 µg Sr.

w) Stock Barium Solution

Dissolve *1.779 gm* of barium chloride ($BaCl_2 \cdot 2H_2O$) in *1,000 ml* of distilled water.
1 ml = 1,000 µg Ba.

x) Stock Gold Solution

Dissolve *1.000 gm* of gold metal in a minimum of aqua regia. Take to dryness, dissolve the residue in *50 ml HCl* and dilute to *1,000 ml* with distilled water. Store in an amber bottle.
1 ml = 1,000 µg Au.

y) Stock Tin Solution

Dissolve *1.000 gm* of tin metal in *100 ml* concentrated *HCl* and dilute to *1,000 ml* with distilled water.
1 ml = 1,000 µg Sn.

z) Stock Titanium Solution

Dissolve *1.000 gm* of titanium metal in *1:1 HCl* with heating. Cool and dilute to *1,000 ml* with *1:1 HCl.*
1 ml = 1,000 µg Ti.

zz) Stock Vanadium Solution

Dissolve *1.000 gm* of vanadium metal in a minimum volume of HNO_3 and dilute to *1,000 ml* with *1%* HNO_3
1 ml = 1,000 µg V.

5. Procedure (Pre-treatment)

I. Wet Digetion (Sulphuric-nitric digestion)

This method of sample preparation is the preferred method for the following types of samples.

1. Turbid or coloured waters.

2. Coloured industrial wastes.

3. Oily samples.

4. Sludge or organic mud samples.

5. Routine aqueous samples of all types.

THE DIGESTION IS SUITABLE FOR THE DETERMINATION OF ALUMINUM, CADMIUM, CHROMIUM, COBALT, COPPER, IRON, LITHIUM, MANGANESE, MOLYBDENUM, NICKEL, SILVER, STRONTIUM, TITANIUM, VANADIUM, ZINC. IT IS NOT SUITABLE FOR THE ANALYSIS OF BARIUM, CALCIUM, GOLD, LEAD, MANGESIUM OR TIN.

Method

1. A sufficient aliquot of sample is pipetted or measured via a graduated cylinder into the digestion vessel. A graduated cylinder is preferred to a pipette for samples in which the suspended solids settle out too quickly to accurately pipette an aliquot. The digestion vessel is usually either a *250 ml* Pyrex beaker, a *100 ml* Pyrex beaker, a *125 ml* Phillips beaker or a *125 ml* Erlenmeyer Flask. The aliquot chosen depends on many variables such as sample source, ions being analyzed, etc. The following are some guidelines for choosing the aliquot size:

   a) Sewage - if thick, *5 to 10 mls* is sufficient; if fairly clear, *50 ml*. If clear take *100 ml*.

   b) Industrial effluents - if clear take *100 ml*; otherwise take smaller volume.

   c) Water samples - usually *100 ml*.

   d) River samples - usually *100 ml*.

   e) Sediment samples - accurately weigh approximately *0.5 grams* of dry sediment into either a *125 ml* Phillips beaker or a *100 ml* Pyrex beaker. Wet the sediment with about *5 or 10 mls* of distilled water.

2. A sample duplicate (if required) is pipetted into a vessel similar to that in *#1*, and similar treatment is given a standard which contains a known amount of each metal being requested on the sample, and a blank containing a volume of distilled water equal to the volume of sample.

3. Pipette *2 ml conc.* H_2SO_4 *and 5 ml conc.* HNO_3 into the reaction vessel, add *2 or 3* antibumping granules, swirl to mix the acids and sample, cover with a watch glass and place on a hot plate.

   As the digestion proceeds, the volume decreases and salt concentration increases. As the volume becomes quite low (*25 ml*) the samples must be watched very closely as bumping causing sample loss can occur.

   The sample is digested until copious white fumes of SO_3 are evolved. If coloured material still persists at this time it may be removed by the careful addition of *2 - 3 drops conc.* HNO_3.

   CAUTION: VERY VIGOROUS REACTION OCCURS UPON ADDITION OF HNO_3

   The samples are removed from the hot plate and allowed to cool. The watch glass and cover are washed down with about *10 ml* distilled water and the beakers returned to the hot plate, brought to boiling and removed. The purpose of this procedure is to dissolve any slowly soluble salts.

   The samples are allowed to cool and transferred by rinsing with distilled water to a *50 ml* digestion tube calibrated at *25 and 50 ml*. The sample is made up to the appropriate mark with distilled water. The tube is covered with parafilm, mixed by inversion and submitted for AAS analysis.

II. Wet Digestion (aqua regia)

This method of sample preparation is suitable for the following types of samples.

1. Turbid or coloured waters.
2. Coloured industrial wastes.
3. Oily samples.
4. Sludge samples.

5. Sediments.

6. Routine aqueous samples of all types.

THE DIGESTION IS SUITABLE FOR THE DETERMINATION OF ALUMINUM, BARIUM, CADMIUM, CALCIUM, COBALT, COPPER, GOLD, LEAD, LITHIUM, MAGNESIUM, MANGANESE, MOLYBDENUM, NICKEL, LITHIUM, TIN, TITANIUM, VANADIUM AND ZINC. AQUA REGIA MUST NOT BE USED FOR IRON OR SILVER ANALYSES.

Method

The procedure is very similar to I. with the exceptions noted:

CAUTION: AQUA REGIA IS A YELLOW, FUMING, CORROSIVE VOLATILE LIQUID WITH A SUFFOCATING ODOUR AND MUST BE KEPT LOOSELY STOPPERED IN A FUME HOOD.

1. Pipette *9 ml HCl (conc.) and 3 ml* HNO_3 *(conc.)* into the reaction vessel.

2. Although no copious white fumes are given off, completion of the digestion is indicated by the clarity of the sample and the colour of the vapours leaving the sample.

3. The samples are treated the same as in I., after digestion is complete.

III. Wet Digetion (nitric-perchloric acid)

THIS METHOD OF SAMPLE PREPARATION IS USED WHEN THE METHODS OUTLINED PREVIOUSLY ARE INADEQUATE. IT IS USED ROUTINELY FOR FISH MUSCLE TISSUE, AND OTHER HIGH PROTEIN MATRICES.

The procedure is very similar to I., with the exceptions noted:

CAUTION: WHENEVER SAMPLES MUST BE DIGESTED USING PERCHLORIC ACID, THEY SHOULD ALWAYS BE BOILED WITH NITRIC ACID PRIOR TO THE ADDITION OF PERCHLORIC ACID.

1. Use a maximum of *2 mls* perchloric acid at any given time.

2. The end point in the digestion comes when copious white fumes are evolved. (this is

also the point at which explosions with the perchloric acid can occur!).

3. The samples are treated the same as in I. after digestion is complete.

IV. Preconcentration ("Clean" Water Samples)

THIS METHOD OF SAMPLE PREPARATION IS PREFERRED WHEN EXTREMELY LOW LEVELS OF HEAVY METALS ARE EXPECTED IN REASONABLY CLEAR LOOKING WATER SAMPLES. THE DIGESTATE IS ANALYZED BY ROUTINE AAS.

THIS PROCESS CONCENTRATES THE SAMPLES BY A FACTOR OF 20, DIGESTS MINOR AMOUNTS OF ORGANIC MATERIAL AND STABILIZES ANY ACID-INSOLUBLE RESIDUE PRIOR TO ATOMIC ABSORPTION MEASUREMENT.

Method

1. *500 ml* of sample is measured into either a *600 ml or 1,000 ml* beaker.

2. A sample duplicate (if required) is measured into a second beaker.

3. Measure *5 mls* of concentrated nitric acid into the beaker and add *2 - 3* anti-bumping granules. Mix well by swirling the contents.

4. Cover each beaker with a speedi-vap cover. This minimizes losses and cross-contamination. Place beakers on a hot plate set at *100-130°C*. as the process proceeds, the volume will decrease, the acid concentration will increase, and the salt concentrations will increase. Most of the organic components in the sample will be volatilized in gaseous form.

5. When the volume is approximately *5-10 mls*, the process should be complete. This is usually indicated by a clear and sometimes slightly coloured solution. If the solution goes dry by accident, add about *5 mls* of concentrated hydrochloric acid to re-dissolve any oxides which have formed.

6. The whole process must be carried out with blanks and at least one standard (containing the metals under investigation) for each run of samples which are pre-concentrated.

7. The digestate is then carefully rinsed with distilled water into a *25 ml* folin digestion tube which is appropriately labelled. The volume is made to the mark and the sample submitted for absorption analysis.

V. Lithium Metaborate Fusion

THIS METHOD OF SAMPLE PREPARATION IS A PROCEDURE FOR THE DISSOLUTION OF SEDIMENTS, ROCKS, SLURRIES, AND SLUDGES WHEN A TRULY TOTAL ANALYSIS IS REQUIRED AND WHERE THERE IS A STRONG LIKELIHOOD OF SOME OR ALL OF THE ELEMENTS BEING TIED UP IN A SILICATE MATRIX.

Method

1. About *1 to 2 grams* of sample (dried at about *60°C* in a vacuum oven) is ignited in a muffle furnace at *500°C*. The ignition loss is noted.

2. About *0.2 grams* of ignited sediment is weighed accurately into a COORS crucible, *1.4 grams* of lithium metaborate flux is placed in the crucible and the contents intimately mixed with a fine-polished glass stirring rod.

3. Transfer this mixture into a graphite crucible prepared for fusion as follows:

   (i) New Crucibles

   These must be pre-ignited at *950°C for half an hour*, then cooled. Take note that the powdery inside surface is not to be disturbed.

   (ii) Crucibles used at least once

   If the crucibles are clean inside, proceed and re-use as many times as possible. However, if there is any material sticking to the inside, clean with fine sand paper. Rub the inner surface with a finger until the surface is shiny. Re-ignite the crucible before fusion at *900°C for about twenty minutes*. Again, take special care not to distrub the powdery inner surface.

4. Place the graphite crucible and contents into a muffle furnace (Thermolyne 1300 as previously noted under Apparatus) for exactly *15 minutes*. After the *15 minutes* period, swirl the crucible with the special tongs to collect all the small beads of fusion, melt

into *one* large bead and very quickly dump the contents into approximately *70-80 ml* of *1:24 v/v* nitric acid contained in a *100 ml* Pyrex beaker. This should be done as quickly as possible to prevent the melt from sticking inside the crucible.

5. Introduce a Teflon-coated stirring bar of length slightly smaller than the diameter of the bottom of the beaker and use a magnetic stirrer to dissolve the flux. The length of this bar is important.

   IF THE SAMPLE IS HIGH IN COPPER, SILVER, OR CHROMIUM (PERCENTAGE LEVELS) THERE MAY BE SOME DIFFICULTY IN DISSOLVING FLUX. IF THERE IS SOME DIFFICULTY, IT MAY BE NECESSARY TO HEAT THE SOLUTION WITH SOME HYDROCHLORIC ACID. PREPARE A SPECIAL BLANK IF THIS PROCEDURE IS CARRIED OUT.

6. Transfer the solution quantitatively to a *200 ml* volumetric flask and dilute to the mark with *1:24 v/v* nitric acid. There may be some needle-like crystals and black particles left undissolved. The crystals are excess metaborate, and the black particles are bits of carbon from the graphite crucibles.

7. The solution is now ready for flame atomic absorption analysis.

VI. Analysis of Prepared Solutions by Atomic Absorption

The following is a guide to the operation of the Varian Techtron AA-4 and AA-5. These are both single beam units. The operating parameters are to be used only as a guide. The optimum conditions must be worked out for each atomic absorption unit, regardless of model or make.

1. Turn on the machine as follows:

   a) mains
   b) readout section (recorder or printer may be attached here)
   c) hollow cathode lamp current supply.

   ALLOW AT LEAST 15 MINUTES WARM UP. BE SURE THAT THERE IS ADEQUATE WATER IN THE WASTE TRAPS.

2. Set the following parameters to their predetermined optimum values:

   a) slit width
   b) lamp current
   c) burner height
   d) primary absorption wavelength
   e) coarse gain

   Refer to Table II.

3. Set mode to % transmittance and tune in the wavelength exactly by turning the monochromator slowly by hand, until the percent transmittance reaches a peak. This indicates the operating wavelength.

4. Switch mode to absorbance.

5. Turn the air (support) pressure on and adjust to the recommended value.

6. Turn on the acetylene to near the recommended value and light the flame. Set the acetylene flow to the exact value specified.

7. Set the blank value by aspirating fresh distilled, deionized water into the flame and turning the fine gain control until the absorbance reads *zero*.

8. Optimizing the Output Signal

   This next step requires experience with atomic absorption. The ultimate goal is to obtain a maximum output (absorbance) for a given concentration of a given element. Once the optimum conditions are obtained, the parameters are noted and should not change radically from day to day, for any given element.

9. In order to read out directly in concentration or onto a recorder, the pertinent accessory is attached to the read-out section of the instrument. All the data presented in summary Table II. is based on direct readout in the concentration mode. In order to obtain a readout directly in concentration, press the concentration button on the printer and adjust the readout by turning the concentration dial until correct concentration is reached. Other samples at or near this concentration may be measured. If the samples do not fall in the range of the standard used, the machine must then either be set up using

a standard with a much higher concentration for the element under test, or the sample must be diluted so that it may be measured without recalibration of the instrument.

10. The total or soluble element concentration in the original sample is calculated as follows:

$$mg/l \text{ desired element} = \frac{mg/l \text{ in prepared solution}}{f}$$

where f is a factor which accounts for the amount of original sample taken for the determination.

11. When turning off the instrument, it is important to turn off the fuel before the air supply.

6. Calculation and Reporting

Calculation formuale are quoted as steps in the procedure.

Results are usually reported to the nearest *0.01 or 2* significant figures at higher concentrations. (See Table I for detection limits).

Preconcentration allows for a *twenty-fold* lowering of detection limits. Results are reported to the nearest *.001.* No more than *two* significant figures are quoted at any time.

7. Precision and Accuracy

See Table I.

These data are reported from *30* determinations on different days of control samples.

TABLE II

AAS INSTRUMENTAL PARAMETERS

Metals	Lamp Current mA	Primary Wavelength Å	Slit Width *	Coarse Gain *	Acetylene Flow *	Support Gas	Support Gas Pressure (PSI)	Instru-ment	Notes
ALUMINUM	10	3093	50	4	8.5	N_2O	21 (6.5)	AA4 AA5	5% K added
CALCIUM	5	4227	25	11	2.3	Air	20	"	1% La added
CADMIUM	3	2288	100	15	1.7	Air	20	"	
COBALT	4	2407	50	17	2.0	Air	20	"	
COPPER	3	3247	25	9	1.5	Air	20	"	
CHROMIUM	10	3579	100	2	8.5	N_2O	21 (6.5)	"	5% K added
IRON	6	2484	25	16	2.9	Air	20	"	
LEAD	5	2170	100	17	2.8	Air	20	"	**
	5	2833	100	10	3.0	Air	20	"	**
LITHIUM	4	6708	100	8	2.3	Air	20	"	
MAGNESIUM	5	2852	25	11	1.9	Air	20	"	1% La added
MANGANESE	9	2795	50	15	2.4	Air	20	"	
MOLYBDENUM	13	3133	100	62	9.2	N_2O	21 (6.5)	"	5% Al added
NICKEL	7	2320	25	16	2.9	Air	20	"	
SILVER	4	3281	50	12	1.5	Air	20	"	
STRONTIUM	6	4607	100	2	8.0	N_2O	21 (6.5)	"	5% K added
ZINC	5	2139	100	15	1.7	Air	20	"	
BARIUM	25	5540	2	--	55	N_2O	30 (40)	PE503	5% K added
GOLD	8	2430	4	--	32	Air	30 (55)	PE503	Background Correction
TIN	4	2250	160	600	8	N_2O	13	IL251	Background Correction
TITANIUM	40	3650	3	--	55	N_2O	30 (40)	PE503	5% Al added
VANADIUM	40	3180	4	--	55	N_2O	30 (40)	PE503	5% Al added

* Units Instrument Dependant

** The absorption at 2203 is subtracted from the absorption at 2170 when the 2170 line is used.

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DATE DUE
